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COMPLETE SPECIFICATION.

Improvements relating to Alkyd Resins and Compositions Containing these.

We, SCHENECTADY CHEMICALS INC., a Corporation duly organised and existing under the laws of the State of New York, of Schenectady, New York State, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to new water-soluble alkyd resins and coating compositions containing these.

The water-soluble alkyd resins according to the invention are condensation products of (a) trimellitic acid, trimesic acid or hemimellitic acid, (b) a saturated aliphatic dicarboxylic acid and (c) a saturated aliphatic dihydric alcohol. Suitable dicarboxylic acids include adipic acid, azelaic acid, sebacic acid, malonic acid, succinic acid, glutaric acid, pimelic acid and suberic acid, while examples of saturated aliphatic dihydric alcohols include ethylene glycol, propylene glycol, 1,3-butylene glycol, trimethylene glycol, 2,2-diethylpropanediol-1,3, neopentyl glycol and hexyleneglycol.

In preparing the water-soluble alkyd resins according to the invention one may use an anhydride instead of the free tricarboxylic acid, for example trimellitic anhydride or di-trimellitic anhydride. The ratio by weight of tricarboxylic acid (or anhydride thereof) to dicarboxylic acid may vary from 1:9 to 9:1. In general, from 1 to 2 equivalents of alcohol are used for each equivalent of total carboxylic acid groups available. Up to 70% by weight of the dihydric alcohol may be replaced by an aromatic or hydroaromatic dihydric alcohol such as *p*-xylylene glycol, hydrogenated Bisphenol A and 1,1¹-isopropylidene-(*p*-phenyleneoxy)-di-2-propanol.

The alkyd resin is conveniently produced by heating the reactants together until the desired acid number is reached. The resins should advantageously have an acid number between 30 and 200, and preferably between 40 and 100 at 100% solids (or between 20 and 50 at 50% solids).

The water-soluble alkyd resins according to the invention form valuable coating compositions in association with other water-soluble resinous products, and as a further feature of the invention we provide a composition comprising an alkyd resin according to the invention together with a water-soluble phenol-formaldehyde resin, a water-soluble ketone-aldehyde resin or a water-soluble aminoplast resin, or a mixture of two or all of these resins. Of the total resin solids content of such a composition, the alkyd resin (or polyester) conveniently forms from 40 to 99%, and preferably from 60 to 90%. The water-soluble phenol-formaldehyde resin may be used in a concentration up to 30% and, when present, is preferably used in an amount of from 10 to 20%. From 0 to 30%, and preferably from 5 to 20%, of the resin content of the composition may be made up by the ketone-aldehyde or aminoplast resin or both.

The water-soluble aminoplast can be a methylol urea such as sesquimethylol urea,

dimethylol urea, or a water-soluble urea-formaldehyde resin, a water-soluble etherified urea-formaldehyde resin, e.g. the methyl ether of a water-soluble urea-formaldehyde reaction product or a methylol melamine, e.g. trimethylolmelamine, hexamethylolmelamine, dimethylolmelamine, an etherified melamine-formaldehyde condensation product, e.g. the trimethyl ether of trimethylolmelamine, the hexamethyl ether of hexamethylolmelamine, or a water-soluble melamine formaldehyde resin.

To improve the wetting and flow properties of the compositions according to the invention and also the continuity of the coating films produced with them it has been found desirable to add methyl cellulose and tall oil to the compositions. The methyl cellulose (dry basis) is preferably used in an amount by weight of from 1 to 10% of the total resin solids, while the corresponding amount of tall oil is preferably 0.5 to 5% by weight. It is found that the use of methyl cellulose and tall oil largely eliminates eyeholing, cratering and pinholing when the compositions are applied to a metal, such as tinplate and aluminium.

The *p*H of the coating compositions according to the invention will generally be between 7 and 10, and is preferably maintained between 8 and 9.5.

The compositions of the present invention are particularly useful in coating the inside of metal cans since they impart no taste to food products in them. However, they can also be used to coat copper wires, vinyl plastic sheets, linoleum and other floor covering materials and wallpapers. Furthermore, they can be used to impregnate paper for making industrial filter paper, and as a cork binder. The coatings obtained are characterised by a high degree of heat-resistance.

The products of the present invention also have excellent adhesion to vinyl resins, e.g. vinyl chloride resins, and it is therefore possible to apply a polyvinyl chloride or a vinyl chloride-vinyl acetate copolymer coating, for example, on top of a coating obtained with a composition according to the invention.

The following six examples illustrate polyesters according to the invention, and were prepared by reacting trimellitic anhydride, adipic acid and the appropriate dihydric alcohol or alcohols at 135–190° C. until the indicated acid number and viscosity were reached, using water as the solvent. The viscosity is expressed in accordance with the Gardner-Holdt Table, which is listed for example in "Physical and Chemical Evaluation of Paints, Colors and Driers" by Gardner-Sward (10th Edition, 1946, Bethesda, Maryland, U.S.A.).

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Trimellitic anhydride (g.)	792	792	693	693	693	792
Adipic acid (g.)	202	202	177	177	177	202
Propylene glycol (g.)	750	574	574	488	488	702
Neopentyl glycol (g.)		164				164
1,1[1] - isopropylidene - (*p* - phenyleneoxy) - di-2-propanol (g.)			133			
p-Xylylene glycol (g.)				259		
Hydrogenated Bisphenol A (g.)					443	
Viscosity	Z-8	Z-3–Z-4	R	U-V	V	D-E
Solids (% in water as solvent)	50	34.5	18	33	19	37.5
Acid No. (at 50% solids)	32.6	33.6	37	63	36.9	33

All of the resins prepared in Examples 1—6 were suitable for mixing with a water-soluble aminoplast and a water-soluble phenol-formaldehyde resin to form coating compositions according to the invention.

The following examples illustrate such compositions, in which all proportions are by weight.

	Ex. 7.	Ex. 8	Ex. 9	Ex. 10
Aqueous polyester of Ex. 1				85
Aqueous polyester of Ex. 2	85	92	90	
Aqueous phenol-formaldehyde	15	10	11	15
Aqueous melamine-formaldehyde	10	8	10	—
Methyl cellulose, 400 cps. (2½% aqueous solution)	7.5	7.5	7.5	5
Ammonium (28% aqueous)	2.5	2.5	2.5	—
Tall oil	0.82	0.82	0.82	—
Water	10	10	10	10

The phenol-formaldehyde employed was that sold under the trade name Bakelite BRL-1100 having a 64—68% solids content.

The melamine-formaldehyde employed in Examples 7, 8, and 9 was that sold under the trade name Reichold's Super Beckamine 3560—65, a water-soluble condensate having a 62—65% solids content.

EXAMPLE 11.

Aqueous polyester of Ex. 2 ...	90
Aqueous phenol-formaldehyde (Bakelite BRLA-1030, 64—68% solids)	10.4
Aqueous melamine-formaldehyde (Super Beckamine 3560—65) ...	10
Methyl cellulose, 400 cps. (2½% aqueous solution)	7.5
Tall oil	0.82
Ammonia (28% aqueous)	2.5
Water	30.4

EXAMPLE 12.

Aqueous polyester of Ex. 2 ...	90
Bakelite BRL—1100	11
Beckamine P-468	9.3
Methyl cellulose, 400 cps. (2½% aqueous solution)	7.5
Ammonium (28% aqueous) ...	2.5
Ricinoleic acid	0.82
Water	10

Beckamine P-468 is a water-soluble acetone-formaldehyde resin having a solids content of 68—72%.

EXAMPLE 13.

Aqueous polyester of Ex. 1 ...	90
Bakelite BRL-1100	11
Beckamine P-426	13
Methyl cellulose, 400 cps. (2½% aqueous solution)	7.5
Methyl diethanolamine	2.5
Tall oil	0.82
Water	27.4

Beckamine 426 is a water-soluble urea-formaldehyde resin having a 48—52% solids content.

EXAMPLE 14.

Aqueous polyester of Ex. 1 ...	90
Bakelite BRL-1100	11
Beckamine P-426	13
Methyl cellulose, 400 cps. (2½% aqueous solution)	7.5
Methyl diethanolamine	2.5
Tall oil	0.82
Water	27.4

The coating compositions of Examples 7—14 were baked on tinplate at 400° F. for 10 minutes to give films of 0.1—0.3 mil. thickness. There was no slivering of the fimls when the coated tinplate was punched out on the press.

The film thickness was generally such that the weight per 4 square inches was between 8 and 15 mg. and generally between 11 and 13 mg.

The baked finishes did not soften and there was no visible effect upon immersing them for one hour in boiling water or after 90 minutes in a pressure cooker at 250° F. and 15 psi. There was no failure in the scorch test for 15 seconds at 740° F. In this respect the coatings were superior to conventional oleoresinous coatings and epoxy resin coatings which did not withstand 3 seconds at 740° F. in the scorch test.

The baked films also had excellent adherence to vinyl resins, e.g. vinyl chloride resins.

WHAT WE CLAIM IS:—

1. A water-soluble alkyd resin comprising the polymeric ester of (a) trimellitic acid, hemimellitic acid or trimesic acid, (b) a saturated aliphatic dicarboxylic and (c) a saturated aliphatic dihydric alcohol.

2. A resin according to Claim 1 in which the ratio by weight of tricarboxylic acid to dicarboxylic acid used in its production is from 1:9 to 9:1.

3. A resin according to Claim 1 or Claim 2, in which from 1 to 2 equivalents of dihydric alcohol are used for each equivalent of carboxylic acid in its production.

4. A resin according to any preceding claim in which up to 70% by weight of the aliphatic alcohol is replaced by an aromatic or hydroaromatic dihydric alcohol.

5. A resin according to any preceding claim having an acid number of from 30 to 200 at 100% solids.

6. A resin according to Claim 5 having an acid number of from 40 to 100 at 100% solids.

7. A resin according to any preceding claim in which the dicarboxylic acid is adipic acid, azelaic acid, sebacic acid, malonic acid, succinic acid, glutaric acid, pimelic acid or suberic acid.

8. A resin according to any preceding claim in which the dihydric alcohol is ethylene glycol, propylene glycol, 1,3-butylene glycol, trimethylene glycol, 2,2-diethylpropanediol-1,3, neopentyl glycol or hexyleneglycol.

9. A resin according to Claim 1 substantially as herein described with reference to any of Examples 1 to 6.

10. A composition comprising a resin as claimed in any preceding claim and a water-soluble phenol-formaldehyde resin, a water-soluble ketone-aldehyde resin or a water-soluble aminoplast resin, or a mixture of two or all of these resins.

11. A composition according to Claim 10 comprising from 40 to 99% by weight of

water-soluble alkyd resin, 0 to 30% by weight of phenol-formaldehyde resin, and 0 to 30% by weight of ketone-aldehyde or aminoplast resin or both.

12. A composition according to Claim 11 comprising from 60 to 90% by weight of water-soluble alkyd resin, 10 to 20% by weight of phenol-formaldehyde resin, and 5 to 20% by weight of ketone-aldehyde or aminoplast resin or both.

13. A composition according to any one of Claims 10 to 12 in which the water-soluble aminoplast is a methylol urea, a water-soluble urea-formaldehyde resin, a water-soluble etherified urea-formaldehyde resin, a methylol melamine, an etherified melamine-formaldehyde condensation product of a water-soluble melamine formaldehyde resin.

14. A composition according to any one of Claims 10 to 13 which also includes methyl cellulose and tall oil.

15. A composition according to Claim 14 in which the methyl cellulose is present is an amount of from 1 to 10% by weight of the total resin solids and the tall oil in an amount of from 0.5 to 5%.

16. A composition according to Claim 10 substantially as herein described with reference to any of Examples 7 to 14.

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